Solvolysis of benzylic chlorides with extended charge delocalization. α-*tert*-Butyl(2-naphthyl)methyl, 9-fluorenyl and monosubstituted benzhydryl chlorides

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ABSTRACT: Rate constants of solvolysis of α-*tert*-butyl(2-naphthyl)methyl chloride (**1**), 9-fluorenyl chloride (**2**) and a series of monosubstituted benzhydryl chlorides (**3**) in a wide range of solvents were measured. Grunwald–Winstein-type correlation analysis of log k for **2** and **3** against Y_{BnCl}, with or without nucleophilicity N, yielded less satisfactory linear correlations than that against log $k(\mathbf{1})$. A new scale of solvent ionizing power, Y_{xBnCl}, for the correlation of solvolytic reactivities of benzylic chlorides with extended charge delocalization based on log $k(\mathbf{1})$ was developed. Application to the mechanistic study suggested the solvolysis of **2** and 4-nitrobenzhydryl chloride were non-limiting. Hammett plots against σ^+ constants exhibited more negative ρ values in less nucleophilic solvents. In a benzhydryl chloride containing a strong deactivating substituent, such as 4-nitro, the positive charge delocalizes mainly over the unsubstituted ring in the cationic transition state. The uneven charge distribution was also confirmed by Mulliken population analysis at the level of the RHF/6–31G*//RHF/3–21G$^{(*)}$ basis set for cations. Comparison of the results of correlation analysis using the equation $\log(k/k_0) = mY$ vs the equation $\log(k/k_0) = mY + hI$, and using the equation $\log(k/k_0) = mY + lN$ vs the equation $\log(k/k_0) = mY + lN + hI$ indicated the use of Y_{BnCl} or Y_{xBnCl} could give a better understanding of solvolytic mechanisms than the combinatorial use of Y_{Cl} and I. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: Solvolysis; Grunwald–Winstein-type analysis; Hammett-type analysis; Y_{xBnCl} scale; 1-aryl-1-phenylmethyl cations; Mulliken population analysis

INTRODUCTION

Correlation analyses of solvent effects on solvolytic reactivities with single- or dual-parameter Grunwald–Winstein equation[1,2]

$$\log(k/k_0) = mY \qquad (1)$$
$$\log(k/k_0) = mY + lN \qquad (2)$$

have been widely employed in mechanistic studies. The empirical parameter Y, the solvent ionizing power has been found to be leaving group dependent, and a large number of Y_X scales have been determined.[3] Observations of dispersion in log k–Y_X plots have been interpreted by a possible variation of solvation effects,[4,5] or by mechanistic changes, such as the presence of general base catalysis[6] or ion pair return.[7] Recent studies on the solvolysis of benzylic substrates led to the necessity of establishing new Y_{BnX} scales for benzylic bromides,[8] chlorides,[9] *p*-nitrobenzoates[10] and tosylates.[11] Nucleophilic solvent intervention could be concluded from the observation of depression of the points corresponding to log k measured in ethanol–trifluoro-

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ethanol systems by using equation(1),[8,10] or from the improvement of linear correlations by using equation (2) with an appropriate N scale.[11]

Later work on the solvolysis of substituted naphthylmethyl tosylates indicated the dependence of solvation on the extent of charge delocalization in the cationic transition state.[12] Another approach by Kevill *et al.*[13] was to add a new term, the aromatic ring parameter I, based on the solvolysis of (4-methoxybenzyl)dimethylsulfonium ion, to the original Grunwald–Winstein equations for correcting the observed dispersion:

$$\log(k/k_0) = mY + hI \qquad (3)$$
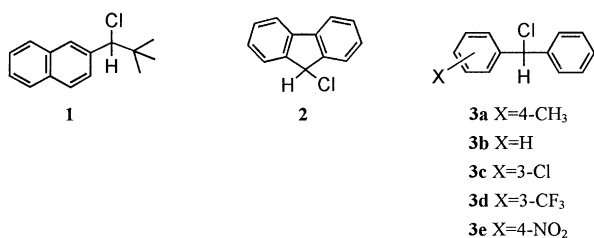$$\log(k/k_0) = mY + lN + hI \qquad (4)$$

More recently, we developed a Y_{xBnBr} scale for the correlation of solvolytic reactivities of bromides, such as benzhydryl bromides, having extended charge delocalization in the transition state.[14] The advantage of using Y_{BnBr} or Y_{xBnBr} [equation (1) and (2)] over Y_{Br} and I [equation (3) and (4)] in correlation analysis has also been demonstrated.[14]

In an extension of our studies on the solvolysis of other benzylic substrates with extended delocalization in the cationic transition state, we found it necessary to establish a similar Y_{xBnCl} scale based on log k values

for α-*tert*-butyl(2-naphthyl)methyl chloride (**1**). Application to the mechanism of solvolysis of 9-fluorenyl chloride (**2**) and benzhydryl chlorides (**3**) is reported in this paper.

1

2

3a X=4-CH₃
3b X=H
3c X=3-Cl
3d X=3-CF₃
3e X=4-NO₂

Figure 1. Correlations of log k for (○) **1** and (Δ) **3d** vs Y_{BnCl}

RESULTS

Chlorides **1–3** were prepared from the corresponding alcohols by treatment with thionyl chloride in carbon tetrachloride. Elemental analyses for new compounds
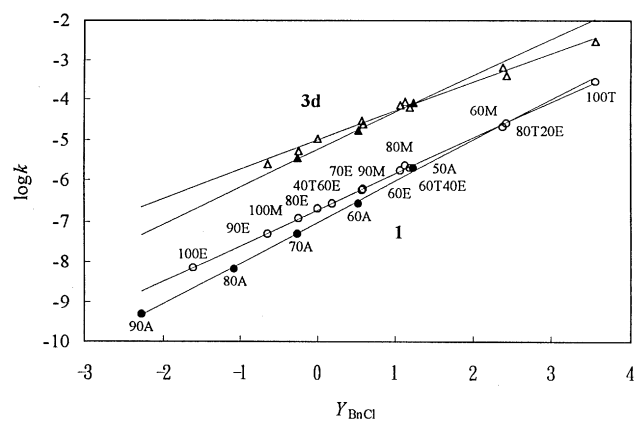
and spectral data for all substrates were found to be compatible with the assigned structures. Conductimetric or, in some cases, titrimetric first-order rate constants

Table 1. Pertinent rate constants for solvolyses of chlorides **1–3**

Solvent[a]	k (25 °C) (s⁻¹)						
	1	**2**	**3a**[b]	**3b**	**3c**	**3d**	**3e**
100E	7.10×10^{-9c}		1.27×10^{-3}	5.42×10^{-5}	1.25×10^{-6d}		4.28×10^{-8d}
90E	4.84×10^{-8c}		1.06×10^{-2}	4.79×10^{-4}		2.49×10^{-6c}	3.43×10^{-7c}
80E	1.99×10^{-7c}	3.01×10^{-7c}	4.20×10^{-2}	1.95×10^{-3}	3.56×10^{-5}	1.06×10^{-5c}	1.30×10^{-6c}
70E	5.90×10^{-7c},	9.23×10^{-7c}		6.03×10^{-3}	9.02×10^{-5}	2.96×10^{-5}	4.59×10^{-6c}
60E	1.71×10^{-6c}	2.93×10^{-6c}		1.59×10^{-2}	3.02×10^{-4}	7.22×10^{-5}	
90A	4.84×10^{-10c}		9.47×10^{-5}	4.40×10^{-6c}			
80A	6.80×10^{-9c}	5.86×10^{-9c}	1.64×10^{-3}	7.17×10^{-5}	1.20×10^{-6c}		
70A	4.94×10^{-8c}	5.09×10^{-8c}	1.21×10^{-2}	5.10×10^{-4}	8.94×10^{-6}	3.43×10^{-6c}	3.39×10^{-7c}
60A	2.72×10^{-7c}	3.19×10^{-7c}	6.16×10^{-2}	2.76×10^{-3}	4.80×10^{-5}	1.68×10^{-5}	1.95×10^{-6c}
50A	1.93×10^{-6c}	2.31×10^{-6c}	6.65×10^{-1c}	1.38×10^{-2}	2.83×10^{-4}	8.07×10^{-5}	9.71×10^{-6}
100M	1.16×10^{-7c}		1.98×10^{-2}	8.10×10^{-4}	1.93×10^{-5}	5.21×10^{-6c}	5.40×10^{-7d}
90M	6.34×10^{-7c}	4.23×10^{-7c}	9.16×10^{-2}	3.65×10^{-3}	9.16×10^{-5}	2.43×10^{-5}	2.51×10^{-6c}
80M	2.26×10^{-6c}	1.48×10^{-6c}	3.26×10^{-1c}		3.14×10^{-4}	8.56×10^{-5}	7.91×10^{-6c}
60M	2.09×10^{-5}	2.13×10^{-5}				6.56×10^{-4}	7.60×10^{-5}
100T	2.82×10^{-4}	5.92×10^{-5}			1.47×10^{-2}	2.99×10^{-3}	5.44×10^{-5}
80T20E	2.53×10^{-5}	9.54×10^{-6c}		1.19×10^{-1}	1.77×10^{-3}	3.84×10^{-4}	1.17×10^{-5}
60T40E	1.97×10^{-6c}	1.38×10^{-6c}	7.57×10^{-1c}	1.47×10^{-2}	2.47×10^{-4}	6.19×10^{-5}	2.52×10^{-6c}
40T60E	2.74×10^{-7c}	2.08×10^{-7c}	7.03×10^{-2}	2.10×10^{-3}			

[a] E = ethanol; A = acetone; M = methanol; T = trifluoroethanol. Numbers represent percentage composition.
[b] Ref. 41.
[c] From Arrhenius plots of data at other temperatures.
[d] Ref. 15.

Table 2. Correlation analyses of log k vs Y_{Cl} and Y_{BnCl}

Parameter		**1**	**2**	**3a**	**3b**	**3c**	**3d**	**3e**
Y_{Cl}	n	18	14	13	15	14	14	14
	m	0.876	0.893	0.794	0.763	0.724	0.694	0.578
	σ[a]	0.100	0.121	0.151	0.110	0.108	0.096	0.067
	r	0.909	0.906	0.847	0.888	0.889	0.902	0.928
Y_{BnCl}	n	18	14	13	15	14	14	14
	m	0.957	0.838	1.03	0.932	0.833	0.745	0.618
	σ[a]	0.028	0.064	0.048	0.04	0.039	0.028	0.061
	r	0.993	0.967	0.988	0.988	0.987	0.992	0.946

[a] Standard deviation.

Table 3. Statistical analyses of the linearity of log k vs Y_{BnCl} for **1** and **3d**

Substrate	Solvent	n	m	σ^a	r	Degrees of freedom	$|t|$ value	CL (%)
1	Aqueous acetone	5	1.02	0.026	0.999	4	11.5	>99.9
	All others	13	0.885	0.007	1.00			
3d	Aqueous acetone	3	0.921	0.020	1.00	6	13.9	>99.9
	All others	11	0.724	0.027	0.994			

[a] Standard deviation.
[b] Confidence limit.

Table 4. Y_{xBnCl} values

Solvent	Y_{xBnCl}	Solvent	Y_{xBnCl}
100E	−1.45	50A	0.987
90E	−0.614	100M	−0.234
80E	0.000	90M	0.503
70E	0.472	80M	1.06
60E	0.934	60M	2.02
90A	−2.61	100T	3.15
80A	−1.47	80T20E	2.10
70A	−0.605	60T40E	0.996
60A	0.136	40T60E	0.139

Table 5. Correlation analyses of log k vs Y_{xBnCl}

	2	**3a**	**3b**	**3c**	**3d**	**3e**
n	14	13	15	14	14	14
m	0.875	1.02	0.954	0.889	0.812	0.682
σ^a	0.050	0.034	0.021	0.020	0.025	0.068
r	0.981	0.994	0.997	0.997	0.994	0.945

[a] Standard deviation.

were measured at least in duplicate. In general, experimental errors within ±2% were observed. Ethanolysis and methanolysis rate constants for **3a–c** are in good agreement (within 5%) with literature data.[15] A larger deviation, however, was found for **3b** in certain aqueous acetone and aqueous ethanol solutions.[5] Pertinent data are given in Table 1.

Regression analyses of log k values against Y_{Cl}[3] showed a poor correlation ($r < 0.93$) in every case. Although **1** and **3d** gave excellent linear correlations ($r > 0.990$) with Y_{BnCl},[9b,16] the results for others were less satisfactory (Table 2). Further, it is obvious from Fig. 1

that there is a separation of the line defined by aqueous acetone and a line defined by other solvents for **1** and **3d**. This could be confirmed by statistical analysis,[17] shown in Table 3.

Similarly to benzhydryl bromides,[14,18] excellent linear relationships were obtained from log k–log k(**1**) plots for **3a–d**. Therefore, a new Y_{xBnCl} scale of solvent ionizing powers based on log k values for α-tert-butyl(2-naphthyl)methyl chloride (**1**) can be developed. The values are given in Table 4 and the results of correlation analysis for **2** and **3** against Y_{xBnCl} using equation (1) are summarized in Table 5.

The observed linear relationships for **3a–d** against Y_{xBnCl} were confirmed by statistical analysis,[17] and representative examples are given in Table 6 and Fig. 2. For both **2** and **3e**, the log k–mY_{xBnCl} plots deviated from linearity and correlation analyses using the dual-
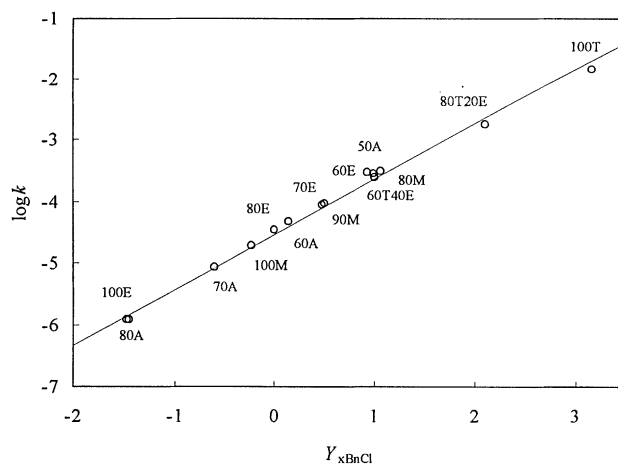
Figure 2. Correlations of log k for (○) **3c** vs Y_{xBnCl}

Table 6. Statistical analyses of the linearity of log k vs Y_{xBnCl} for **3a** and **3b**

Substrate	Solvent	n	m	σ^a	r	Degrees of freedom	$|t|$ value	CL (%)[b]
3a	Aqueous acetone	5	1.05	0.022	1.00	10	0.770	<80
	All others	8	1.03	0.068	0.987			
3d	Aqueous acetone	3	0.860	0.037	0.999	3	1.73	<85
	All others	11	0.820	0.029	0.994			

[a] Standard deviation.
[b] Confidence limit.

Table 7. Correlation analyses of log k vs different Y and N

Substrate	Y, N	n	m	σ^{a}	l	σ^{a}	r
2	Y_{BnCl}, N_T	14	1.03	0.068	0.295	0.079	0.986
	Y_{xBnCl}, N_T	14	0.991	0.055	0.186	0.063	0.990
	Y_{BnCl}, N_{OTs}	13	1.00	0.056	0.351	0.081	0.988
	Y_{xBnCl}, N_{OTs}	13	0.990	0.036	0.261	0.051	0.995
3e	Y_{BnCl}, N_T	14	0.869	0.066	0.375	0.082	0.982
	Y_{xBnCl}, N_T	14	0.914	0.085	0.320	0.095	0.973
	Y_{BnCl}, N_{OTs}	13	0.843	0.037	0.473	0.059	0.993
	Y_{xBnCl}, N_{OTs}	13	0.912	0.052	0.444	0.074	0.985

[a] Standard deviation.

Table 8. Hammett-type analyses against σ^{+} constants

Solvent	n		σ^{a}	r
100E	4	−4.11	0.077	1.00
80E	5	−4.20	0.091	0.999
70E	4	−4.06	0.279	0.995
70A	5	−4.21	0.088	0.999
60A	5	−4.18	0.099	0.999
50A	5	−4.40	0.186	0.997
100M	5	−4.20	0.060	1.00
90M	5	−4.19	0.064	1.00
80M	4	−4.26	0.040	1.00
80T20E	4	−5.12	0.266	0.997
60T40E	5	−4.93	0.117	0.999

[a] Standard deviation.

Table 9. Comparison of k values in solvents with similar Y but different N values

|	k (25 °C) (s^{-1})^{a}		
Substrate	50A^{b}	60T40E^{c}	Rate ratio
3a	6.65×10^{-1}	7.57×10^{-1}	0.878
3b	1.38×10^{-2}	1.47×10^{-2}	0.938
3c	2.83×10^{-4}	2.47×10^{-4}	1.15
3d	8.07×10^{-5}	6.19×10^{-5}	1.30
3e	9.71×10^{-6}	2.52×10^{-6}	3.61

[a] From Table 1.
[b] $Y_{xBnCl} = 0.987$; $Y_{BnCl} = 1.23$.
[c] $Y_{xBnCl} = 0.996$; $Y_{BnCl} = 1.18$.

parameter equation (2) against Y_{xBnCl} or Y_{BnCl}, and N_T[19] or N_{OTs}[20] [equation (2)] were carried out. The results are given in Table 7.

Hammett plots of log k values for **3a–e** against σ^{+} constants;[21]

$$\log(k/k_0) = \sigma^{+}\rho \tag{5}$$

gave excellent linear correlations in a variety of solvent systems (Table 8). Comparisons of solvolytic reactivities in 60% trifluoroethanol–40% ethanol and in 50% acetone are illustrated in Table 9. To estimate the positive charge distribution in carbocation, a number of *ab initio* calculations for cations derived from **3** were carried out. The

Table 10. Calculated atomic charges for cations derived from **3a–e.**
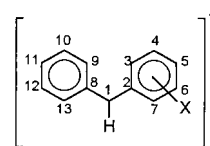
	X				
Carbon	4-Me	H	3-Cl	3-CF$_3$	4-NO$_2$
C-1	0.221	0.232	0.241	0.243	0.250
C-2	−0.055	−0.048	−0.042	−0.054	−0.034
C-3	0.120	0.104	0.138	0.146	0.078
C-4	0.020	0.038	−0.079	−0.098	0.140
C-5	0.223	0.139	0.171	0.180	−0.157
C-6	0.007	0.041	0.052	0.044	0.146
C-7	0.121	0.110	0.101	0.114	0.089
C-8	−0.045	−0.048	−0.050	−0.049	−0.051
C-9	0.088	0.111	0.114	0.114	0.142
C-10	0.036	0.041	0.039	0.040	0.045
C-11	0.126	0.140	0.151	0.153	0.173
C-12	0.040	0.037	0.043	0.044	0.043
C-13	0.097	0.105	0.121	0.124	0.136
Ph^{a}	0.342	0.385	0.418	0.425	0.489
Ar^{b}	0.436	0.383	0.341	0.332	0.261

[a] Total charge on the phenyl ring.
[b] Total charge on the aryl ring.

results of Mulliken population analyses[22] at the level of the RHF/6–31G*//RHF/3–21G$^{(*)}$ basis set are presented in Table 10. Similar results were obtained from molecular electrostatic potential[23] and natural population analysis.[24]

Treatment of rate data for **1–3** with the multi-parameter equations (3) and (4) yielded the results given in Table 11.

DISCUSSION

Solvolysis of secondary α-*tert*-butylbenzyl substrates was in general considered to proceed via a limiting S_N1 mechanism,[11,12,14,18,25–27] with some exceptions such as

Table 11. Correlation analysis against Y_{Cl}, N and I

Substrate	Parameter	n	m	σ^a	h^b	σ^a	l^c	σ^a	r
1	Y_{Cl}, I	17	0.874	0.052	1.72	0.247			0.980
	Y_{Cl}, I, N_T	17	0.926	0.070	1.83	0.263	0.122	0.109	0.982
	Y_{Cl}, I, N_{OTs}	15	0.878	0.074	1.75	0.311	0.113	0.142	0.979
2	Y_{Cl}, I	14	0.863	0.085	1.03	0.283			0.958
	Y_{Cl}, I, N_T	14	1.07	0.093	1.37	0.242	0.314	0.103	0.979
	Y_{Cl}, I, N_{OTs}	13	1.04	0.069	1.50	0.231	0.400	0.103	0.986
3a	Y_{Cl}, I	12	0.898	0.065	1.85	0.253			0.979
3b	Y_{Cl}, I	14	0.801	0.057	1.45	0.236			0.976
3c	Y_{Cl}, I	14	0.726	0.057	1.39	0.245			0.973
3d	Y_{Cl}, I	13	0.705	0.065	1.03	0.224			0.964
3e	Y_{Cl}, I	13	0.581	0.071	0.405	0.328			0.933
	Y_{Cl}, I, N_T	13	0.749	0.103	0.777	0.340	0.277	0.136	0.954
	Y_{Cl}, I, N_{OTs}	12	0.749	0.082	0.949	0.343	0.393	0.150	0.968

[a] Standard deviation.

phenolysis of α-*tert*-butyl(4-methoxy)benzyl *p*-nitro-benzoate[28] and acetolysis of the corresponding chloride.[29] Similarly to the corresponding bromide[14] and tosylate,[12] the solvolysis of α-*tert*-butyl(2-naphthyl)-methyl chloride (**1**) is also likely to involve a limiting mechanism with positive charge delocalization over both rings in the transition state. Although the regression analysis in Table 2 indicated a poor linear correlation with Y_{Cl} ($r = 0.909$) but an excellent linear correlation with Y_{BnCl} ($r = 0.993$) for **1**, an obvious splitting of lines, one for aqueous acetone and one for all others, could be found (Fig. 1). The separation of lines can be confirmed by statistical analysis[17] to have a confidence level greater than 99.99% (Table 3). Similar analysis was also found to be applicable for **3d**. A difference in the solvation of the cationic transition states with different extents of charge delocalization, such as (2-naphthyl)methyl cation (**4**) and benzyl cation (**5**), is the likely explanation as has been suggested in our previous work.[12,14]

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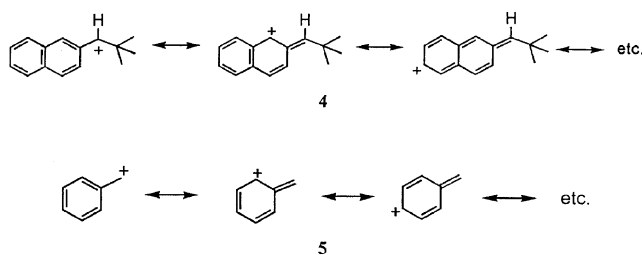
Interesting results were also observed from the solvolysis of 9-fluorenyl chloride (**2**) and monosubstituted benzhydryl chlorides (**3**). Like the corresponding bromides,[14,18,30] good linear relationships could not be found for log k vs Y_{Cl} [equation (1)], as was shown in Table 2. Deviations from linear correlations with Y_{BnCl} were observed for **2,3a–c** and **3e**. A unimolecular mechanism has generally been accepted for interpreting the solvolysis of benzhydryl halides,[15] *p*-nitrobenzo-ates,[31] mesylates[32] and dimethylsulfonium ion,[33] and also the solvolysis of 9-fluorenyl bromide[34] and tosylate.[35] Our recent studies, however, indicated significant nucleophilic solvent intervention in the solvolysis of monosubstituted benzhydryl bromides containing a strong electron-withdrawing group,[14,18] and in the case of 9-fluorenyl bromide.[30] Moreover, a new Y_{xBnBr} scale was found to be necessary to correlate the solvolytic reactivities of **2** and **3**.[14] It seems to be justified to solve the present problem by a similar approach. Excellent linear relationships were obtained from log k vs log $k(\mathbf{1})$ plots for **3a–d,** and a new Y_{xBnCl} scale of solvent ionizing powers based on log k values for **1** could be developed (Table 4).

The results of regression analyses of log k values for **2** and **3a–e** against Y_{xBnCl} using equation (1) are given in Table 5. Excellent linear correlations ($r = 0.994$–0.997) were found for **3a–d.** The results of statistical analysis[17] in Table 6 confirm the linearity of the log k vs Y_{xBnCl} plot for **3a** and **d.** The limiting S_N1 mechanism in the solvolysis of **3a–d** is confirmed by the observed m values of 0.8–1. An example of a Grunwald–Winstein plot [equation (1)] is illustrated in Fig. 2. The application of equation (2) was then examined for **2** and **3e**. It is interesting that despite the claim of a general preference for using N_T in dual-parameter correlations,[19] the data in Table 7 indicate that the use of N_{OTs}[20] would give a better linear correlation and offer a more plausible explanation. For instance, the combination of N_{OTs} and the newly developed Y_{xBnCl} values yielded an excellent linear relationship ($r = 0.995$) with a reasonable l value (0.261) for **2**. Extensive charge delocalization through the whole ring system and the presence of significant nucleophilic solvent intervention at the reaction center in the transition state are likely, as have been found in the solvolysis of 9-fluorenyl bromide.[30]

On the other hand, the use of either N_T or N_{OTs} with Y_{xBnCl} in equation (2) gave less satisfactory linear correlations ($r = 0.97$–0.98 in Table 7) for **3e**. Regression
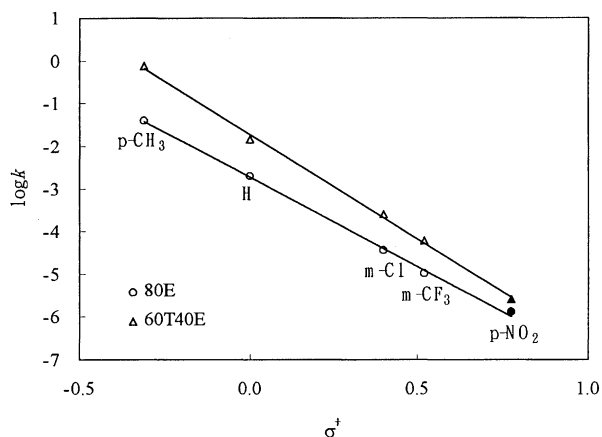
Figure 3. Correlations of log k for **3a–e** vs σ^+ constants

analysis using N_{OTs} and Y_{BnCl} resulted in a linear relationship with $r = 0.993$. Again, similarly to the corresponding bromide,[14] the present finding of a better correlation with Y_{BnCl} than with Y_{xBnCl} may be attributed to the smaller extent of positive charge distribution. It is likely that in a benzhydryl chloride containing strong electron-withdrawing group, such as 4-nitro, the charge delocalizes mainly over the unsubstituted phenyl ring in the cationic transition state. Consequently, Y_{BnCl}, instead of Y_{xBnCl}, is the choice for the correlations.

Previous work on the solvolysis of monosubstituted benzhydryl chlorides showed an excellent linear Hammett-type plot against σ^+ constants, with $\rho = -4.13$ (propan-2-ol), -4.15 (ethanol) and -4.22 (methanol).[15] In the present study, Table 8 also indicates linear log k vs σ^+ plots [equation (5)] with similar ρ values in nucleophilic solvents (-4.10 to -4.26). The ρ value became more negative (-4.93 to -5.12) in the less nucleophilic ethanol–trifluoroethanol solvent systems. Representative examples in Fig. 3 demonstrated increasing reactivities for substrates with a more electron-donating group. Moreover, comparison of the rate constants k in solvents of similar solvent ionizing powers but different solvent nucleophilicities (Table 9) also indicates a greater rate enhancement in the more nucleophilic solvent, 50A, for less reactive substrates. The large influence of solvent nucleophilicity in the case of **3e** might account for the small m value for **3e** in Table 5. Further, the present results give an additional example that the linear relationships against σ^+ constants [equation (5)] are not sensitive to nucleophilic solvent intervention, as has already been noted in *tert*-cumyl systems.[36]

To confirm the above-mentioned difference in positive charge distribution for carbocations generated from different substrates, a number of *ab initio* calculations were carried out. Charges on hydrogens were summed into the attached carbons. The results of Mulliken population analyses[22] at the level of the RHF/6–31G*// RHF/3–21G$^{(*)}$ basis set for 1-aryl-1-phenylmethyl ca-

tions derived from **3a–e** are summarized in Table 10. The positive charge on C-1 is nearly the same for different cations. However, the charge distribution in the monosubstituted aryl ring decreases from 0.436 for 4-methyl to 0.383 for 4-hydrogen, 0.341 for 3-chloro, 0.332 for 3-trifluoromethyl and 0.261 for 4-nitro. In contrast, an increasing order of change in charge distribution is realized in the unsubstituted phenyl ring. More important, more positive charge is found in the aryl ring (0.436) than in the phenyl ring (0.342) for the cation containing an electron-donating 4-methyl group, whereas more positive charge is found in the phenyl ring (0.489) than in the aryl ring (0.261) for the cation containing an electron-withdrawing 4-nitro group. These results of calculations are in harmony with the conclusion drawn from the correlation analyses of solvolytic rate data (see above). In addition, molecular electrostatic potential[23] and natural population analysis[24] gave similar results.[37]

The dual-parameter equation (3) and the multi-parameter equation (4) were also applied to examine the solvolytic behavior of **1–3**. Both N_T and N_{OTs} scales were employed. Since in Table 11 only moderately good linear correlations ($r = 0.95$–0.98) with Y_{Cl} and I, or with Y_{Cl}, I and N_T, were obtained, no close relationship between the outcome of these regression analyses and solvolytic reactivities could be found. Therefore, in addition to the deficiencies already discussed,[38] the present results suggest another disadvantage for using the aromatic ring parameter I in the correlation analysis of reactivities.

EXPERIMENTAL

Capillary melting points are uncorrected. Proton and carbon-13 nuclear magnetic resonance spectra were measured on a Bruker Model AM-300 or AC-200 instrument using tetramethylsilane as internal standard. Infrared spectra were measured using a Perkin-Elmer Model 983G spectrometer. Elemental analyses were performed by the Microanalytical Laboratory at National Taiwan University.

Materials. Solvents for kinetic studies were of spectral or reagent grade and were purified according to standard methods.[39] Reagent-grade solvents and chemicals were used for general purposes. Doubly deionized water was used to prepare aqueous solvent systems for solvolysis.

α-*tert*-Butyl(2-naphthyl)methyl chloride (**1**) was prepared from the reaction of thionyl chloride with the corresponding alcohol, which had been obtained from the Grignard reaction of 2-naphthylmagnesium bromide with 2,2-dimethylpropanoyl chloride in tetrahydrofuran. A white solid of m.p. 74–75 °C and correct elemental analysis (found, C 77.12, H 7.22%; $C_{15}H_{17}Cl$ requires C 77.41, H 7.36%) was obtained.

9-Fluorenyl chloride (**2**), m.p. 149–150 °C (lit.[40] 147–

148 °C) was prepared by the treatment of commercially available 9-fluorenol with thionyl chloride in carbon tetrachloride.

Monosubstituted benzhydryl chlorides **3a–e** were obtained according to the following procedures. Commercially available benzophenones were reduced by sodium borohydride to the alcohols, which were converted into the corresponding chlorides by treatment with thionyl chloride followed by purification by column chromatography or vacuum distillation. 4-Methylbenzhydryl chloride (**3a**), benzhydryl chloride (**3b**), 3-chlorobenzhydryl chloride (**3c**) and 4-nitrobenzhydryl chloride (**3e**) are known compounds.[15] An acceptable elemental analysis (found, C 61.91, H 3.67%; $C_{14}H_{10}F_3Cl$ requires C 62.12, H 3.70%) was obtained for the new compound 3-trifluoromethylbenzhydryl chloride (**3d**).

Infrared, proton and carbon-13 NMR data for **1–3** were found to be consistent with the assigned structures.

Kinetic Measurements. Conductimetric and titrimetric rate constants were measured as described.[9b]

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